Nanoscale Res Lett (2010) 5:1408–1417
DOI 10.1007/s11671-010-9654-6

NANO EXPRESS

Novel Crystalline SiO_2 Nanoparticles via Annelids Bioprocessing of Agro-Industrial Wastes

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Received: 20 April 2009 / Accepted: 17 May 2010 / Published online: 15 June 2010

Abstract The synthesis of nanoparticles silica oxide from rice husk, sugar cane bagasse and coffee husk, by employing vermicompost with annelids (*Eisenia foetida*) is reported. The product (*humus*) is calcinated and extracted to recover the crystalline nanoparticles. X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and dynamic light scattering (DLS) show that the biotransformation allows creating specific crystalline phases, since equivalent particles synthesized without biotransformation are bigger and with different crystalline structure.

Keywords Silica nanoparticles · Worms · Agricultural waste · Bioprocessing

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Introduction

Agro-industrial wastes have recently attracted a great deal of attention as potential sources of novel green alternatives such as biotransformation for fuels and other materials. Many of these wastes contain amorphous silica that can be transformed into crystalline nanoparticles of industrial interest.

Silicon is the most common element of the Earth's surface after oxygen; this element is released into the soil by chemical and biological processes [1]. Industrially speaking, silicon is the basis of semiconductors, glasses, ceramics, plastics, elastomers, resins, mesoporous molecular sieves and catalysts, optical fibers and coatings, insulators, moisture shields, photoluminescent polymers, fillers, cosmetics and biomedical devices [2, 3], among many other applications. The manufacture of these materials typically requires high temperatures, high pressure and/or the use of caustic chemicals [4]. In contrast, in nature, silica architectures with delicate morphologies are generated under ambient conditions [5]. Unicellular organisms, such as diatoms, use structuring and templating biomolecules to produce silica shells that not only contain hierarchically ordered porous structures, with dimensions ranging from the nanometer to the micrometer domain, but also possess remarkable mechanical and structural properties [6–8]. Other approach involves the use *Fosuarium oxysporum*, a plant pathogenic fungus for the biotransformation of naturally occurring amorphous plant bio-silica into quasi-spherical crystalline silica nanoparticles and its extracellular leaching in the aqueous environment at room temperature [9]. An analysis suggested that extreme thermophilic bacteria within the genera *thermus* and *hydrogenobacter* are predominant components among the indigenous microbial community in siliceous deposits.

These bacteria seem to actively contribute to the rapid formation of huge siliceous deposits [10].

In general, the biosilification products are commonly composed of amorphous silica (opal-A, opal-CT and opal-C), and other crystal arrays such as cristobalite, trydimite and quartz. In particular, amorphous silica is a dominant component in marine surface sediment most of which is considered to be generated by the activity of living organism [3, 11]. Many scientists not only investigate the process underlying their formation, but also aim to mimic these processes in order to obtain better control over the structure and morphology of chemically produced silica [12–14]. The natural silica production receives increasing attention, since it holds the key to the formation of silica morphologies with a dedicated organization of hierarchically structure elements and the ability to synthesize such silica under ambient conditions [15]. There exist many studies in silica bio-mineralization of simple aquatic life forms, including unicellular organisms like diatoms, radiolaria and sinurophytes as multicellular sponges [16–19]. In the soil, silica plays a major role in higher plants [20]. Many plants sequester silica in biogenic phytoliths and soils can accumulate significant quantities of biogenic opal-A [21]. The silica absorbed for terrestrial plants is around a fraction of 1% of the dry matter to several percent, and in some plants to 10% or even higher [22]. It is observed that in some grammineae as rice (*Oryza sativa*), silica constitutes 20–22% of its total production in the rice husk form [23]. Sugarcane bagasse contains around 5.08 to 7.08% of silica in dry matter basis [24], and coffee husk contains around 1 to 3% of silica in dry matter basis [25].

It is important to mention that the mechanical strength of plants resides greatly on the cell wall, enabling them to achieve and maintain erect habit conductive to light interception. There exist a relation in plants stress and the increased rigidity of cell walls of plants grown with ample available silica [26, 27]. When plants die, the silica is reincorporated into the soil where microorganisms play an important role in the degradation of organic matter and in the release of minerals nutrients [28, 29], other important source that raises mineralization rate is earthworms producing biohumus. Humus contains principally carbon, oxygen, hydrogen and minor proportion of other minerals. These elements vary within the humic material in order to define chemical characteristics of the original basis. There exists a symbiotic interaction between earthworms and microorganisms that breakdown and fragment the organic matter progressively, finally incorporating it into water-stable aggregates. The mineral nutrients in earthworm casts and lining earthworm burrows are in a form readily available to plants. There is evidence that interactions between earthworms and microorganisms not only provide these available nutrients, but stimulate plant growth indirectly in others ways [30]. The digestive system of earthworms consists of a pharynx, esophagus and gizzard (zone reception) followed by an anterior intestine that secrets enzymes and a posterior intestine that absorb nutrients. During progress through this digestive system, there is a dramatic increase in numbers of microorganism of up to 1,000 times. The digestive systems of earthworms from different species, genera and families differ in detail, but their gusts have a common basic structure. In different species earthworms *Eisenia foetida* is peculiar for its degradation rate [28]. Most studies of digestive enzymes in earthworms have been limited to the lumbricids. Protease, lipase, amylase, lichenase, cellulose and chitinase activities also have been described [31]. A wide range of microorganisms, including bacteria, algae, protozoa, actinomycetes, fungi and even nematodes, are found commonly throughout the length of the earthworms gut. The species of microbes in the gut are usually very similar to those in the surrounding soil or organic matter upon which the earthworms feed [32–34]. *Eisenia foetida* is considered a machine to produce humus in conditions environmental control and the microorganism can live in it in anoxic effect raising productivity in the material expel. The biological mechanism to earthworms transforms organic matter and even so carries out biosilification even is uncertain. Understanding the mechanism of silica nanofabrication in other organisms is supported by a precursor namely biosilica monosilicic acid $Si(OH)_4$ [35, 36]. Proteins have been isolated from diatoms, sponges and grasses that are proposed to be responsible for biosilification and have been sequenced and some of the key amino acids identified. Other authors have studied the role of homopolymers of various amino acids that are key constituents of the proteins lysine, histidine, arginine, cysteine, proline and serine in the process biosilification [37]. This biopolymer acts as gelating agents of silica oligomers in silicic acid and as flocculation agents in silica sols [38, 39]. Other researches have been focused toward the development of efficient and innovative fabrication methods to obtain inorganic materials using microorganisms from potential cheap agro-industrial waste materials and could lead to an energy-conserving and economically viable green approach toward the large-scale synthesis of oxide nanomaterials [9]. Thus, we develop a novel process for synthesis of diverse nanometric materials with specific crystal arrays as precursors to agro-industrial wastes employing annelids, an approach not used before, that permit to rise natural sources dedicated to production particles' mean biosilification.

Experimental

Three sources derived from agro-industrial activity were used: rice husk, coffee husk and sugarcane bagasse. These by-products were added to vermicompost separately. The

annelid specimen used was *Eisenia foetida.* The environmental conditions ideal to the reproduction and control of these specimens were set up: temperature at 20°C, moisture around 60–85%, aeration conditions and darkness. The stabilization time was around 1 month and the humus obtained was dried in a room at a temperature between 30 and 40°C. Then, the humus was sieved to size 0.5 mm approximately. Next, the sample was calcinated to eliminate the organic matter. Three temperature levels were used: 500, 600 and 700°C for each agro-industrial waste by 19 h. Calcinations were carried out in a muffle Lindberg/Eurotherm model 847 with energy consumption of 0.17 kcal/h cm^3, considering that the average density of the nanoparticles is around 0.1380 g/cm^3, the consumed energy in the calcinations is approximately 1.2318 kcal/h by each gram of recuperated SiO_2 particles. This energy could be considered low in comparison with other conventional process where fumed silica is manufactured with a consumed energy of until 15.48 kcal/h by each gram of SiO_2 particles [40]. Thus, the samples were tried with nitric and hydrochloric acids (volume ratio 3:1). For each gram of calcinated sample, 4 ml of acid mix was added in order to eliminate impurities (calcium, potassium, magnesium, manganese, iron, boron and phosphorous). Acid treatment was achieved at 40°C by 4 h with constant stirring. Then, samples were filtrated and washed with distilled water to neutralize them. Solids obtained were dried at room temperature. All reagents employed were provided by Sigma–Aldrich.

Also, as a reference, SiO_2 was obtained from the agro-industrial wastes without employing vermicompost bioprocess. The extraction process to recuperate SiO_2 is the same as described previously using calcination and acid treatment. In addition, commercial synthetic SiO_2 Aerosil® 130 provided by Degussa AG was employed to compare size and structure with SiO_2 nanoparticles produced in this research. Aerosil® 130 particles are amorphous SiO_2 nanoparticles produced by high-temperature hydrolysis of silicon tetrachloride in an oxygen gas flame [41]. Also, this research compares the particle features based on biotransformation process with those synthesized using chemical process.

SiO_2 powders were characterized by employing a Fourier transform infrared spectrophotometer (FTIR) Bruker Vector 33 using KBr powders. Transmission electron microscopy (TEM) was realized using a JEOL TEM-1010 transmission electron microscope, and high-resolution transmission electron microscopy (HRTEM) was realized in a Tecnai G2 T20 Microscope. Average particle size was determined for dynamic light scattering (DLS) using a Brookhaven model BI200SM with laser He–Ne of 35 mW model 9167 EB-1 Melles-Griot. Elemental analysis was carried out using energy dispersion spectroscopy (EDS) mean software Oxford Inca X–Sight. EDS is adapted in equipment JEOL JSM-6060 LV Scanning Electron Microscope. X-ray diffraction (XRD) was realized in a diffractometer Rigaku, model MiniFlex, with a wavelength from 1.54 Å corresponding kα cupper radiations. Crystalline structures present in the samples were analyzed with Materials Data Jade software of MDI Materials Data.

Results and Discussion

Figure 1 shows the FTIR spectroscopy analysis to the samples obtained from the agro-industrial wastes: rice husk, coffee husk and sugarcane bagasse after vermicompost bioprocess, calcinations and extraction process. The spectra present three important bands that allow identifying the SiO_2. At 1,080 cm^{-1}, a band corresponds to stretching antisymmetric mode of Si–O–Si group. Around 800–810 cm^{-1}, bending vibration mode is detected. This peak corresponds to Si–O group. Also, the peak observed at 500 cm^{-1} corresponds to rocking mode of the Si–O group. At 3,500 and 1,640 cm^{-1} are observed stretching vibration mode of O–H and twisting vibration mode of H–O–H, respectively. The peaks formed at different temperatures of calcination (500, 600 and 700°C) do not show important differences in the infrared analysis. The FTIR results suggest that carbon from the organic matter is removed. Thus, silica is released, and then the suboxides found after calcinations are separated correctly. In addition, the SiO_2 typical bands represent strong evidence of the efficiency in the synthesis process based on biotransformation with annelids. Also, the bands corresponding to O–H vibration mode and H–O–H twisting vibration mode indicate that particles synthesized remain hydrated. As can be observed in Fig. 1, commercial sample Aerosil® 130 shows the same three bands corresponding to SiO_2. However, the peaks at 3,500 and 1,640 cm^{-1} are weaker than the peaks belonging to the samples synthesized using vermicompost. The latter allows to assume that nanoparticles obtained by vermicompost are further hydrated than Aerosil®130 particles. This could be important for developing hybrid materials, inasmuch as these types of materials use silanol groups to attach organic moieties to inorganic Si [42–45].

Figures 2 a–f show TEM images for the SiO_2 particles obtained using the synthesis by vermicompost. The morphology and structure of these particles is not completely spherical. In addition, several particle clusters are observed in these images. This agglomerates show different shapes of nanometric size. Figure 2 g–h shows SiO_2 particles obtained from the agro-industrial wastes without biotransformation. In these pictures are observed elliptical particles with different diameter and a relatively bigger size than particles analyzed in the Fig. 2 a–f. This reveals that

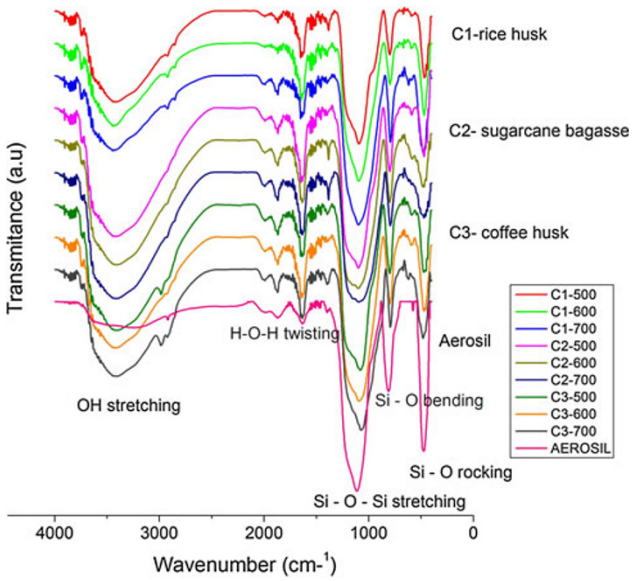

Fig. 1 IR bands to synthesis of nanoparticles SiO_2 obtained for vermicompost. The Figure show the bands more representatives to SiO_2 to in rice husk, sugarcane bagasse and coffee husk at temperature of calcination: 500, 600 and 700°C. Representative bands for Aerosil® 130 too are shown

bioprocesses employed contribute to reduce the size in SiO_2 particles. We suggest that this size reduction is induced in earthworm gut with the contribution from several microorganisms. Figure 3 a–b shows HRTEM images of SiO_2 particles obtained through bioprocess. In these images, it is possible appreciate the SiO_2 particles in an atomic scale. Nanometric size and crystal structure are observed in these images. Thus, it is shown that these particles present as well a crystalline structure contrary to amorphous synthetic SiO_2. In addition, the Fig. 3 shows the diffraction patterns and Miller index corresponding with these structures in a selected area (A). Figures show the nanoparticles obtained from the precursors that contain a higher content of SiO_2, such as rice husk (Fig. 3a) and sugarcane bagasse (Fig. 3b). The indexation of nanoparticles obtained from rice husk shows SiO_2 with crystal arrangement related to α hexagonal quartz with the next lattice parameters: 0.340 nm (1−1 0 0), 0.243 nm (1 1−2 0) and 0.198 nm (2 0−2 0). In the case of nanoparticles obtained from sugarcane bagasse, SiO_2 posses a tetragonal arrangement with the next lattice parameters: 0.200 nm (2 0 0), 0.199 nm (0 2 0) and 0.142 nm (2 2 0). In accord with these results, it is possible to suppose an important contribution of the vermicompost bioprocess in order to give crystalline phases in SiO_2 nanoparticles.

In order to confirm the TEM and HRTEM results, particle size was analyzed employing dynamic light scattering (DLS). The results obtained by this technique are summarized in Table 1. The mean diameter of particles synthesized employing bioprocess is around 81 nm and do not show polydispersity. In contrast, the mean diameter of particles synthesized without using bioprocess is between 152 and 254 nm with low polydispersity. This is in agreement with TEM and HRTEM images and confirms the contribution of bioprocess in particle size reduction to achieve a nanometric range. It is important to emphasize the presence of agglomerates in the particles obtained without biotransformation, which are not observed in the particles obtained by employing bioprocess. Thus, as well as the bioprocess contribution to particle size reduction also provides specific arrangement to the particles. It is suggested that this effect is produced by the microorganisms which are part of metabolism in the earthworm. The size and morphology of particle in the biosilification process are related with the concentration of inorganic phosphate and polyamines, both compounds play an important role in order to catalyze the polycondensation of silanol groups [46]. In vermicompost, the concentrations of these compounds vary with the microbial population. Thus, it is supposed that the size and morphology of SiO_2 nanoparticles could be changed in this kind of bioprocess.

Table 2 shows the elemental analysis for SiO_2 particles synthesized by bioprocess; a significant amount of silicon and oxygen weight percent is observed in all samples obtained with the precursors employed: 41.62% Si and 52.90% O for particles obtained from rice husk; 23.37% Si and 42.37% O in particles synthesized from sugarcane bagasse and 41.68% Si and 55.39% O to particles extracted from coffee husk. Also, in the composition are observed other elements with lower percent than silica and oxygen, such as sodium, magnesium, aluminum, potassium and calcium. These elements are typical in the biomineralization process and take part in the crystalline phases growing that are produced with this biological mechanism.

Figure 4 shows the diffractograms generated from the particles obtained using the three precursors: rice husk (a–b), sugar cane bagasse (c–d) and coffee husk (e–f). Crystalline nanoparticles are obtained using two different calcination temperatures: 500°C (a, c and e) and 700°C (b, d and f). Figure 4a shows the diffractogram corresponding to particles obtained from rice husk at 500°C. In this figure, it is observed an amorphous structure when the bioprocess is not used during the synthesis. In contrast, crystalline phases are found when the bioprocess is employed. In this diffractogram, it is possible to identify typical peaks corresponding to diffraction planes from quartz and other polymorphic structures of SiO_2, such as trydimite. Also, erionite and albite diffraction planes corresponding to aluminum silicate groups are found. These results support the proposal that biomineralization mechanism is achieved through earthworms contributing in the atomic arrangement and modifying the original structure toward specific

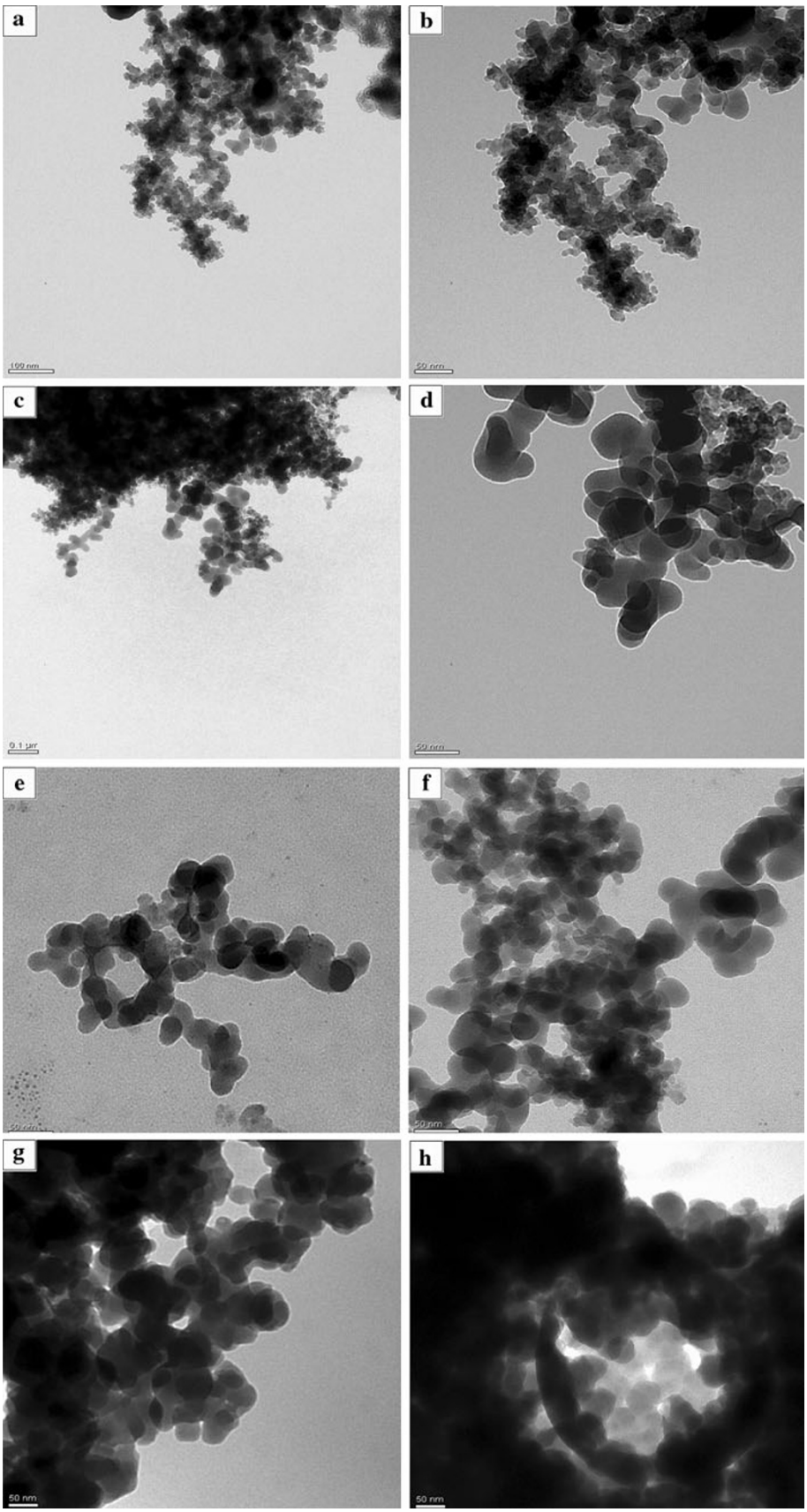

Fig. 2 TEM images to synthesis of SiO_2 obtained with bioprocess (**a**–**f**) and without bioprocess (**g**–**h**). Figure 2 shows differences in size, form and dispersity to nanoparticles synthesized for both methods employed, with bioprocess (**a**–**f**) and without bioprocess (**g**–**h**)

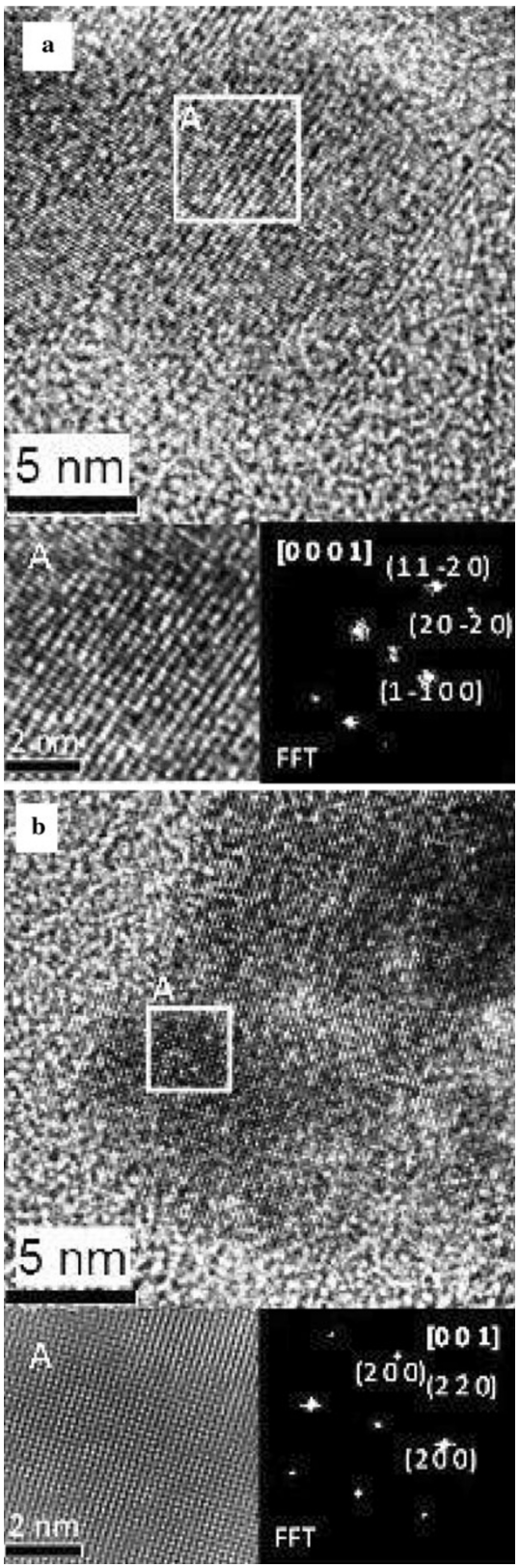

Fig. 3 HRTEM images and indexation of SiO_2 nanoparticles obtained by bioprocess: **a** nanoparticles obtained from rice husk **b** nanoparticles obtained from sugarcane bagasse

crystalline structures. Figure 4b shows the diffractrogram corresponding to particles obtained from rice husk at 700°C. In spite of the high temperature, even amorphous structure is observed when bioprocess is not used and only one diffraction plane corresponding at low quartz is shown. This crystal is formed probably by temperature effect. In the same Fig. (4b), it is shown the diffractrogram corresponding to the samples treated with bioprocess at 700°C. In this figure, the crystalline structure is related to low quartz, trydimite and albite.

Figure 4c and d show the diffractrograms corresponding to particles obtained from sugarcane bagasse. Crystalline phases are present in both procedures (with and without bioprocess). However, some diffraction planes are not the same in both processes. This allows to assume that the calcination temperature and earthworm metabolism play an important role to generate different crystalline phases that involve not only silicon and oxygen atoms, but other elements take part, as well. In Fig. 4c and d, by comparing the diffractrograms (samples obtained without bioprocess at 500 and 700°C), it is possible to observe that the same crystalline phases are found: quartz (different crystallographic planes) and trydimite. However, the diffractrograms corresponding to samples obtained via bioprocess show different crystalline phases, such as: zinc phosphate, aluminum phosphate at 500°C and albite in 700°C.

It is important to mention that silica shows several polyphorms depending on temperature and pressure. Thus, although bioprocess conditions employed to obtain SiO_2 particles are favorable to inducing α hexagonal quartz (corroborated by X-ray diffraction), it is possible to find others metastable polyphorms such as tetragonal arrangement (268–1,470°C). This structure belongs to β crystobalite [3]. Therefore, some SiO_2 nanoparticles obtained from sugarcane bagasse can be found with transitions of hexagonal to tetragonal phase. Thus, tetragonal arrangement does not appear in X-ray diffraction; however, in some nanoparticles characterized by HRTEM (Fig. 3b) it is identified.

Diffractrograms corresponding to particles obtained from coffee husk are shown in Fig. 4e and f. Significant changes in both processes (using bioprocess and without employing bioprocess), which are produced by temperature and metabolism in earthworms, are observed. At 500°C, by employing bioprocess, the diffraction peaks detected are related to quartz, trydimite, sanidine and magnesium nickel hydride, meanwhile without bioprocesses diffraction peaks appear, corresponding to trydimite, gypsum and calcium aluminim oxide hydrate. At 700°C, by employing bioprocess, quartz, aluminim phosphate and caminite are found, meanwhile without bioprocess appears: calcium aluminim oxide hydrate, trikalsilite and quartz.

Table 1 Diameter mean using DLS to particles SiO_2 synthesized with bioprocess and without bioprocess

Sample	With bioprocess		Without bioprocess	
	Diameter mean (nm)	Variance relative	Diameter mean (nm)	Variance relative
Rice husk	81.1	0.018	233.4	0.025
Sugarcane bagasse	81.1	0.041	185.1	0.000
Coffee husk	81.8	0.014	152.6	0.036
Aerosil® 130	–	–	75.8	0.000

Table 1 shows variations in mean diameter in nm and variance relative to particles SiO_2 synthesized since precursors: rice husk, sugarcane bagasse and coffee husk with bioprocess and without bioprocess. A comparative with Aerosil® 130 too is presented

Table 2 EDS to particles SiO_2 synthesized with bioprocess and without bioprocess

Rice husk			Sugarcane bagasse			Coffee husk		
Element	% weight	% Atomic	Element	% weight	% Atomic	Element	% weight	% Atomic
O K	52.90	66.82	C K	31.35	42.02	O K	55.39	68.88
Na K	0.350	0.310	O K	42.37	42.91	Na K	0.540	0.470
Mg K	0.790	0.650	Na K	0.410	0.290	Al K	0.510	0.380
Al K	1.030	0.770	Al K	1.140	0.690	Si K	41.68	29.52
Si K	41.62	29.95	Si K	23.37	13.48	K K	0.900	0.460
K K	1.390	0.720	K K	0.680	0.280	Ca K	0.330	0.160
Ca K	0.450	0.250	Ca K	0.610	0.250	Mo L	0.650	0.130
Ti K	0.350	0.150	Fe K	0.280	0.080			
Fe K	1.120	0.410						
Total	100.0		Total	100.0		Total	100.0	

Table 2 shows EDS analysis in percent weight and percent atomic to nanoparticles SiO_2 employing bioprocess in rice husk, sugarcane bagasse and coffee husk

Table 3 shows the crystallization percent, considering precursor type and calcination temperature employed. Crystallization degree is obtained for both: particles obtained via bioprocess and particles synthesized without using bioprocess. These values are calculated by considering mean low curve area in the peaks from XRD. It is observed that, for rice husk, the effect in the temperature is not enough as to transform the amorphous phase. However, the metabolic effect in earthworms increases the crystalline phase up to 28.47% (500°C) and 16.69%(700°C). In sugarcane bagasse, the effect is the opposite, the crystalline phase is low for the samples obtained via bioprocess and crystallinity percent increases for particles obtained without bioprocess. In addition, diffractograms obtained from sugarcane bagasse show that some crystalline phases do not correspond to SiO_2, such as zinc phosphate and aluminim phosphate; however, when the bioprocess is not used, particles show a considerable number of SiO_2 polymorphs. This suggests that most of the oxygen needed to form SiO_2 may be consumed by the earthworms during their metabolic process. This assumption is in agreement with EDS analysis, inasmuch as EDS results for particles obtained from sugar baggasse show lower percent of oxygen than particles synthesized from rice husk and coffee husk. With respect to the crystallization percent in the particles obtained from coffee husk, there is not a clear tendency. For the samples obtained using bioprocess at 500°C, the crystallization percent is lower than that of samples synthesized without bioprocess. Probably, bioprocessing contributes to provide certain array in the nanoparticles, depending on organic matter, oxygen and other inorganic compounds present in the precursors. This would confirm that temperature is not the most important factor for the crystallinity in these kinds of nanoparticles.

Conclusion

The microbial population in annelids is very important to achieve the biotransformation of the amorphous silica naturally present in the analyzed agro-industrial wastes. Characteristics of the organic matter exposed to a broad variety of microorganisms, as well as the method employed for the fragmentation and minerals release, represent key factors to understand the biocrystallization. Our results reveal a novel synthesis method to obtain SiO_2 crystalline

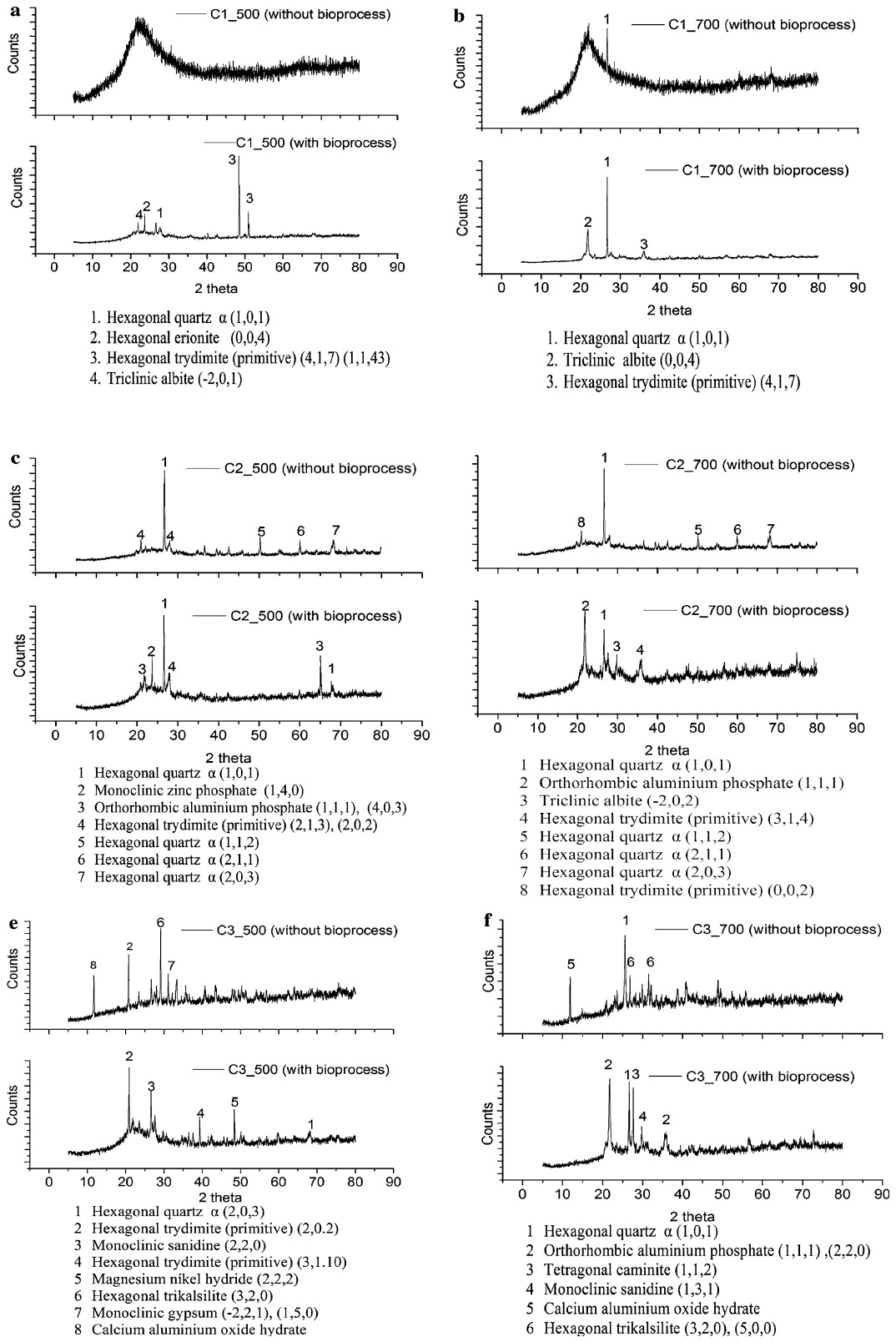

Fig. 4 X-ray diffraction to synthesis of nanoparticles SiO_2 obtained with bioprocess and without bioprocess using as precursors: rice husk (**a**–**b**) sugarcane bagasse (**c**–**d**) and coffee husk (**e**–**f**) to two temperatures of calcinations: 500 and 700°C. It shows a change in the crystallinity of the nanoparticles synthesized, since the different precursors used and varying the temperature of calcination and employing or not employing the bioprocess

Table 3 Percent crystallization in particles SiO_2 synthesized with bioprocess and without bioprocess

Sample	Crystallization (%)			
	With bioprocess		Without bioprocess	
	500°C	700°C	500°C	700°C
Rice husk	28.47	16.69	0.000	1.910
Sugarcane bagasse	10.42	9.190	76.12	13.71
Coffee husk	15.73	25.82	58.28	17.36

In this table is presented an estimative obtained for low curve areas in the peaks of XRD. These percents shows the contribution than the temperature of calcination and the bioprocess have on the crystallization of nanoparticles of SiO_2

nanoparticles using annelids' biotransformation by employing agro-industrial wastes. The approach represents an inexpensive and relatively eco-friendly technology in comparison with standard chemical methods. By taking into account the biological aspects of the production of SiO_2 nanoparticles with specific crystal arrangement using annelids allows to extend the number of living organism dedicate to biosilification, in addition to open an interesting field toward the knowledge of new annelid bioprocesses with a primitive metabolism, as potential alternative natural nanotechnology bioprocesses to synthesize nanoparticles and nanostructures, for the particles obtained through biotransformation by annelids show similar characteristics than synthetic SiO_2 Aerosil®130 such as size, composition and polydispersity. While synthetic particles possess amorphous structure the particles synthesized using vermicompost present different disables characteristics such as crystalline (different polymorphism) and nanometric dimension.

Acknowledgments The authors are grateful to Ms. Maria de Lourdes Palma for her assistance in TEM, to Dr. Genoveva Hernández-Padron for her assistance in IR analysis, to Dr. Eric Rivera for his assistance in XRD, to CINVESTAV Querétaro, particularly to Dr. S. Jimenez and Mr. F Rodriguez for their assistance in some measurements and to DGEST and Consejo Nacional de Ciencia y Tecnologia (CONACyT), Mexico, for the economical support through the projects P333-05 and JI-58232, respectively. Financial support from the National Council for Science and Technology of Mexico (CONACYT) (PhD Scholarship to A.E.-G.) is gratefully acknowledged.

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